Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

EMULSION STABILITY OF MINE HYDRAULIC FLUIDS UNDER FREEZE-THAW CYCLES

N.K. Sarin
Canadian Explosive Atmospheres Laboratory

October 1984

This document is an unedited interim report [illegible] to [illegible] represent a final [illegible] the opinion of [illegible] for Mineral and [illegible] (CANMET)

Ce rapport est un rapport [illegible] non révisé et rédigé [illegible] pour fin de [illegible] et de documentation [illegible] ne représente nulle[illegible] opinion définitive de [illegible] Centre canadien de [illegible] technologie des minéraux et de l'énergie (CANMET)

19 AP

MICROMEDIA

ENERGY RESEARCH PROGRAM
MINING RESEARCH LABORATORIES
DIVISION REPORT ERP/MRL 84-98(TR)

EMULSION STABILITY OF MINE HYDRAULIC FLUIDS UNDER FREEZE-THAW CYCLES

by

N.K. Sarin*

ABSTRACT

The report shows that the number of freeze-thaw cycles and subsequent storage time at room temperature has a direct influence on the magnitude of the oil and water separations in the water-based emulsion type fire-resistant hydraulic fluids.

It is recommended that a minimum of seven freeze-thaw cycles should be used to properly identify separation stability of emulsion fluids instead of two cycles presently being used in accordance with the CSA draft standard M423.

It is also proposed to change the existing acceptance criteria of CSA standard to a more realistic level, i.e., the water separation limit should be increased to 3%, and the oil separation limit should be decreased to less than 2%. Supporting data, tables and graphs are also included.

---

*Investigation Officer, Canadian Explosives Atmospheres Laboratory, Mining Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

STABILITÉ DES FLUIDES HYDRAULIQUES ÉMULSIFIANTS DES MINES DANS DES CONDITIONS DE GEL ET DE DÉGEL

par

N.K. Sarin*

RÉSUMÉ

Le présent rapport démontre que le nombre de cycles de gel et de dégel ainsi que la durée de la période de stockage ont des répercussions directes sur l'ampleur du processus de séparation d'huile et d'eau dans les fluides hydrauliques réfractaires de type émulsifiant à base d'eau.

On recommande d'utiliser au moins sept cycles de gel - dégel afin d'identifier de façon précise la stabilité de séparation des fluides émulsifiants au lieu des deux périodes que l'on utilise actuellement conformément à la norme M423 de l'ACNOR.

On suggère également d'adapter le critère de normalisation actuel de l'ACNOR de façon plus réaliste, i.e., en augmentant la limite de séparation d'eau à 3 % et en diminuant la limite de séparation d'huile à moins de 2 %. Le rapport présente également des données, des tableaux et des diagrammes à l'appui de ces recommandations.

*Agent d'investigation, Laboratoire de recherche sur les atmosphères explosives, Laboratoires de recherche minière, CANMET, Énergie, Mines et Ressources Canada, Ottawa.

CONTENTS

	Page
ABSTRACT	i
RÉSUMÉ	ii
INTRODUCTION	1
BACKGROUND	1
Test Procedure	2
Test Equipment	3
OBSERVATIONS AND DISCUSSIONS	3
CONCLUSION	6
Recommendations	6
ACKNOWLEDGEMENTS	7
REFERENCES	8

TABLES

No.		
1.	Percentage separation using uncovered cylinders	9
2.	Percentage separation using covered cylinders	10
3.	Comparative freeze-thaw test using covered and uncovered cylinders	11

FIGURES

1.	% Oil separation using uncovered cylinders	12
2.	% Water separation using uncovered cylinders	13
3.	% Oil separation using covered cylinders	14
4.	% Water separation using covered cylinders	15

INTRODUCTION

In a mine hydraulic system, power is transmitted by means of fluid media which must be acceptable from a safety and an operational point of view. With the introduction of fire-resistant hydraulic fluids in Canadian mines, water-based invert emulsion type hydraulic fluids appear to be more popular than other types. These fluids are chosen due to their relatively lower costs and increased fire-resistance achieved with the water content ranging between 37% and 45% by volume; the upper limit being controlled by the desired lubricity. Although 95% water content is normal in the case of static applications, e.g., mine roof supports, etc., the major problem has been their limitation in high pressure dynamic systems and extreme temperature conditions. In northern Canadian mines, the temperatures can drop below -50°C. Most emulsion type fluids have a tendency to separate into water and oil layers when subjected to extreme hot and cold treatment whether they be used in mining machinery in open pit mines of the north or kept in an open storage. A certain amount of oil separation, i.e., 1-2% is desirable to prevent evaporation of water content during warm conditions. Water being heavier than oil generally stays at the bottom layer and the combustible portion of the emulsion separates on the top. The mine operators are liable to pour out the combustible portion of the oil from the drums for charging the hydraulic systems. Even though the drums bear instructions to mix well before use, this practice may not be satisfactory when the water content has already separated and frozen at the bottom layer. Consequently, a flammable oil may be charged to the mining machine, thereby posing a safety threat to the mining personnel.

It is therefore essential to develop suitable tests and control the use of unstable fire-resistant fluids in order to minimize the probability of fire-hazards in a mining environment.

BACKGROUND

The Canadian Explosive Atmospheres Laboratory (CEAL) has been using a freeze-thaw stability test in accordance with the CEAL Report 80-101, "Interim certification requirements for the fire-resistant hydraulic fluids," the acceptable separation level being 3% in either case i.e., water or

oil, (3). This report was published in July 1980, prior to the formation of the CSA committee on hydraulic fluids, and it specified two cycles of freeze-thaw. This was accepted by the CSA committee. The CSA standard M423 specifies an acceptance limit of 3% and 1% separation for oil and water respectively, however one member of the Steering Committee has questioned the validity of two cycles. For this reason, a revision of CSA standard M423 is under consideration. We at CEAL are obliged to investigate the influence of several cycles of freeze-thaw on the separation properties of various emulsion fluids because CEAL staff has assisted in the formulation of the CSA standard.

CEAL followed the Factory Mutual Research Corporation (FMC) test procedure for hot and cold stability tests with the exception that CEAL uses two cycles instead of ten cycles in a freeze-thaw test. The National Coal Board (NCB) specifies (1) daily temperature cycling between -5°C and 5°C or -10°C and 0°C as opposed to -40°C and room temperature used by CEAL and FMC. The medium-term stability is an additional requirement of the NCB specification where the separation is noted after 1000 h of storage at room temperature following their standard temperature cycle; however no mention is made of the number of freeze-thaw cycles employed.

At FMC the measurement of magnitudes of separations is done after the fluids are subjected to a centrifugal action for 6 min, following the completion of the freeze-thaw test, whereas the CSA standard does not mention any mechanical agitation of the samples prior to observing the separation levels.

TEST PROCEDURE

A 100 mL sample of each of the nine certified emulsion fluids were poured into open graduated cylinders and subjected to -40°C for a duration of 16 h and then kept at room temperature (21°C ± 2°C) for 8 h to complete one freeze-thaw cycle. This was repeated for five such cycles and then stored for 1000 h at room temperature. Magnitudes of water and oil separations were measured at the end of two cycles, five cycles and subsequent storage for 48 h and 1000 h.

After having examined the results of Table 1, it was suspected that due to the sudden environmental change from -40°C to room temperature, some water condensation could occur inside the open-mouth cylinders and thereby adulterate the natural water separation levels. A comparative test was then

carried out on two separate emulsions using covered and uncovered cylinders under a standard freeze-thaw cycle repeated 3 times. Separation values after each cycle and subsequent 48 h storage indicated slightly more water separation in the uncovered cylinder. This resulted in repetition of the initial test on the same 9 fluids however using covered cylinders. The separation values were recorded afer each freeze-thaw cycle for the ten consecutive cycles (see Table 2).

As a standard procedure the cylinders were rinsed thoroughly with tap water and isopropyl alcohol respectively and then dried with compressed air before charging the test fluid at room temperature. Each fluid container was thoroughly agitated before drawing a sample for the test.

The cylinders were covered with glass stoppers.

For this investigation, only fresh samples as received from the manufacturer/client were used.

TEST EQUIPMENT

1. Graduated transparent glass cylinders approximately 25 cm tall and 2.5 cm diameter both open and closed mouth types were used. Glass stoppers were used as the covers. The cylinders are marked at each ml level. Therefore the accuracy of measurement with the naked eye is 0.5 mL at best.
2. The freezer unit is 1.0 cubic meter capacity capable of generating -40°C and is produced by "HOTPACK" in Waterloo, Ontario. Thermal capacity of the unit is 117 watts per hour at -67°C.

OBSERVATIONS AND DISCUSSIONS

Before attempting an analysis of the test results it is important to mention that due to the initial procedural difficulties, the data in Tables 1 and 3 are not fully reliable and should not be compared to data in Table 2, however, we have included Fig. 1 and 2 only for an indication of a general trend of water-oil separations. In the subsequent tests a proper procedure for flushing and cleaning of cylinders was adopted besides covering them with glass stoppers. Consequently most of the quantitative conclusions and recommendations are based on data from Table 2 and the corresponding Fig. 3 and 4.

Figures 1 and 2 indicate that both oil and water separations increase with the increase in the number of freeze-thaw cycles and with the storage time after the fifth cycle. Although the influence of storage time is quite pronounced in some cases, Table 1 indicates that one minute of mechanical agitation after 1000 hr storage would significantly reduce the magnitudes of separation below the current acceptance limits, however, in one out of six fluids, the water separation remained above the acceptance limit. Therefore mechanical agitation can not be relied upon fully in field use. Besides agitation does not assist below freezing temperatures.

It is also noticed from Fig. 3 and 4 that all of the fluids tested would pass the CEAL stability criteria for oil and water separation when only two cycles are used in a freeze-thaw test. In the case of oil content, separations remained steady under 1.5% after the fourth cycle for all the fluids. It is preferable to have small proportion of oil separation on the top in order to prevent water evaporation under heated conditions in a machine, however, excessive separations are undesirable in case a mine operator invertently removes the top layer (combustible portion) for adding to a machine without fully agitating the storage drum. The CSA standard M423 specifies an oil separation limit of 3% which appears to be a little loose considering that all test fluids exhibited separation under 1.6% even up to the tenth freeze-thaw cycle. Also, most fluids reached their maximum separation level of 1.5% at the end of the fifth cycle.

On the other hand water separations for six out of ten fluids increased steadily forming an S curve and tending to level out at the tenth cycle, however none of the fluids indicated any separation at the end of the second cycle. Only two fluids crossed 1% level up to the end of the fourth cycle and only one fluid reached the 3% level at the end of the fifth cycle. By the end of the seventh cycle most fluids reached the 3% separation limit used by "CEAL" interim requirements prior to its replacement by the CSA standard M423.

Obviously then, use of only two cycles in a standard freeze-thaw cycle is not adequate to determine emulsion stability with certainty. Perhaps for these reasons, FMC uses a minimum of ten freeze-thaw cycles (2) with the same temperature limits and the exposure times as in a standard cycle. Apparently they are looking for the peak separations which seems to occur at or around the tenth cycle in most cases. Since the FMC standard is not limited

to mining applications, the equipment performance is equally important apart from safety considerations of fire-resistance. In the case of mining environment, therefore, one might ask as to what is the maximum percentage of water separation which may be tolerated without sacrificing the fire-resistance? This would require extension of the present investigation to evaluate flammability of fluids after we have established a standard freezethaw test; however, experience in our laboratory suggests that emulsion type fluids generally contain 37% to 43% water content and emulsions containing less than 35% water generally do not meet the fire-resistance requirements when subjected to a spray ignition test as described in the CSA standard. This favours a higher limit on water-separation instead of 1% prescribed by CSA standard M423. Further, it is obvious from Fig. 4 that most fluids exhibit a separation more than 2% at the end of fifth freeze-thaw cycle. Comparatively, FMC approval standard 6930/75 specifies an oil separation limit of 3% but makes no mention of the water-separation (2).

It is also observed from Fig. 4 that three out of ten fluids did not separate at all even at the end of the tenth cycle. It can be inferred that technology does exist which can provide freeze-thaw stability far beyond two cycles presently used in the standard. It is also implied that an optimum number of cycles lie between five and ten and a separation limit of 3% for water and 2% for oil appears more realistic based on the results of this investigation. No significant advantage is gained beyond the end of the fifth cycle in the case of oil and beyond the end of the seventh cycle in the case of water. Since both are evaluated in a common test, it is appropriate to accept minimum of seven cycles for the evaluation of freeze-thaw stability. Using this criteria, with 1% or 3% limit on water separation, only three of ten fluids would meet the requirement. Should we increase the minimum number of cycles to ten, three of ten fluids would still meet the requirement for a separation limit of either 1% or 3%. On the other hand, if five cycles are used, with 1% limit on water separation, 50% of the fluids would meet the requirement and if the limit is increased to 3%, as much as eight of ten fluids would be acceptable.

One could also argue that a minimum of ten cycles is more realistic choice, considering the logic of FMC and results from Fig. 4 where the separations level out after the tenth cycle, although no significant advantage for pass or fail appears beyond the seventh cycle.

The other major consideration is the lowest temperature of -40°C in the test. The environmental temperatures could fall far below -40°C in some of the open pit mines in northern Canada. A case can be made therefore, in support of investigating lower temperature limits in the freeze-thaw cycle described above. This is intended to cover the worst possible situation in a Canadian mining environment; however further research in this aspect must confirm that some advantage can be gained before recommendations are made for a change in the existing CSA standard.

CONCLUSIONS

1. Two cycles used in a freeze-thaw stability test for emulsion type hydraulic fluids are inadequate to properly identify and analyse their stability under cold conditions as outlined in the CSA standard M423.
2. The limits of percentage separation for oil and water in the CSA standard appear to have been mentioned in a reverse order, i.e., 3% limit is somewhat lax for oil and 1% limit for water is too restrictive.

RECOMMENDATIONS

1. The CSA standard M423 should be altered to reflect the following changes:
   a) The minimum number of freeze-thaw cycles in a emulsion stability test be increased from two to seven.
   b) The oil separation limit be changed from 3% to 2%.
   c) The water separation limit be changed from 1% to 3%.
   d) A procedure for cleaning and neutralizing the graduated cylinders before using them for testing the fluid samples should be specified. Stoppers should be mandatory to seal off the cylinders for the duration of the test.
2. The following studies be undertaken as an extension of this investigation:
   a) The effect of agitation on the re-emulsification properties of fluids that have been subjected to a freeze-thaw test.
   b) The influence of long term storage on the separation properties when conducted in a standard laboratory temperature 20 ± 2°C.
   c) The influence of changing the minimum test temperature on the separation properties of emulsion in a freeze-thaw stability test.

3. A clarification should be sought from the CSA Technical Committee on hydraulic fluids regarding transition times for environmental temperature changes between -40°C to 21°C and vice-versa.

ACKNOWLEDGEMENTS

Thanks are extended to Mr. J. Bossert, Manager, CEAL, for his guidance and to Dr. K. Mintz for his constructive comments.

REFERENCES

1. NCB Specification No.: 570/1970. "Fire resistant fluids for use in machinery and hydraulic equipment".

2. Factory Mutual Research; "Approval standard - less hazardous hydraulic fluids; Class No. 6930"; February 1975.

3. Sarin, N.K. and Bossert, J.A. "Interim certification requirements for fire-resistant hydraulic fluids"; Division Report ERP/MRL 80-10(R); CANMET, Energy, Mines and Resources Canada; July 1980.

4. CSA standard M423; "Fire-resistant hydraulic fluids"; March 1984.

Table 1 - Freeze-thaw cycles investigation of water/oil emulsion fluids using uncovered cylinders

(Percentage separation)

Sr #	After 2 cycles		After 5 cycles		48 h after 5th cycle March 20th/84		1200 h after 5th cycle May 7/84		Shake for 1 min record after 48 h		CEAL code
	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water	
1	1.0	nil	1.0	nil	1.0	nil	2.0	5.0	1.0	nil	CEAL sample # 131
2	1.0	nil	1.5	nil	1.5	nil	4.0	nil	1.0	nil	CEAL sample # 132
3	1.0	nil	1.0	5.0	1.0	8.0	2.5	8.0	1.0	2.0	CEAL sample # 134
4	1.0	nil	1.0	<2.0	1.0	2.0	2.0	10.0	1.0	nil	CEAL sample # 135
5	1.0	nil	1.0	<2.0	1.0	2.0	2.0	8.0	nil	1.0	CEAL sample # 136
6	1.0	nil	1.0	6.0	1.0	8.0	3.0	8.5	1.0	1.5	CEAL sample # 137
7	1.0	nil	1.0	nil	1.0	nil	2.0	nil	1.0	nil	CEAL sample # 138
8	1.0	nil	1.0	15.0	1.0	27.0	2.0	27.0	0.5	6.5	CEAL sample # 139
9	1.0	nil	1.0	nil	1.0	nil	3.0	nil	1.0	nil	CEAL sample # 147

Note: The accuracy of readings is ± .5 mL.

Table 2 - Freeze-thaw cycles investigation of water/oil emulsion fluids using covered cylinders

(Percentage separation)

Sr #	CEAL Code	Number of freeze-thaw cycles completed																			
		1		2		3		4		5		6		7		8		9		10	
		Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water
1	#131	0	0	.5	0	1.0	3.0	1.0	6.0	1.5	11.0	1.5	15.0	1.5	18.0	1.5	19.0	1.5	20	1.5	21.0
2	#132	0	0	.5	0	1.0	0	1.5	0	1.5	0	1.5	0	1.5	0	1.5	0	1.5	0	1.5	0
3	#134	0	0	0	0	.5	0	1.5	Trace	1.5	2.0	1.5	5.0	1.5	9.0	1.5	14.0	1.5	16	1.5	18.0
4	#135	0	0	0	0	.5	0	1.0	Trace	1.0	1.0	1.0	2.0	1.0	5.0	1.0	10.0	1.0	15	1.0	16.0
5	#136	0	0	0	0	.5	0	1.0	0	1.0	0	1.0	1.5	1.0	5.0	1.0	10.0	1.5	12.5	1.5	15.0
6	#137	0	0	0	0	.5	0	1.5	Trace	1.5	2.0	1.5	6.0	1.5	10.0	1.5	14.0	1.5	17	1.5	18
7	#138	0	0	0	0	.5	1.0	1.0	2.0	1.0	2.0	1.0	2.5	1.0	3.0	1.0	3.5	1.5	4	1.5	5.0
8	#139	0	0	0	0	1.0	16.0	1.5	18.0	1.5	20.0	1.5	20.0	1.5	20.0	1.5	20.0	1.5	20.0	1.5	20.0
9	#150	0	0	0	0	.5	0	1.5	0	1.5	0	1.5	0	1.5	0	1.5	0	1.0	0	1.0	0
10	#151	0	0	0	0	.5	0	1.0	0	1.0	0	1.0	0	1.0	0	1.0	0	1.5	0	1.5	0

Note: The accuracy of reading is ± .5 mL.

Table 3 - Comparative freeze-thaw test water-based fluids

Covered vs uncovered cylinders

Sr #	CEAL code	Percentage separation								Remarks
		Cycle # 1		Cycle # 2		Cycle # 3		48 h later		
		Oil	H_2O	Oil	H_2O	Oil	H_2O	Oil	H_2O	
1	131	0	0	0.5	0.0	1.0	3.0	2.0	3.0	covered
2	131	0	0	0.5	0	1.0	1.0	2.0	1.0	uncovered
3	139	0	0	0.5	20.0	1.0	20.5	1.5	20.5	covered
4	139	0	0	0.5	22.0	1.0	22.5	1.5	22.5	uncovered

Note: The accuracy of readings is ± .5 mL.

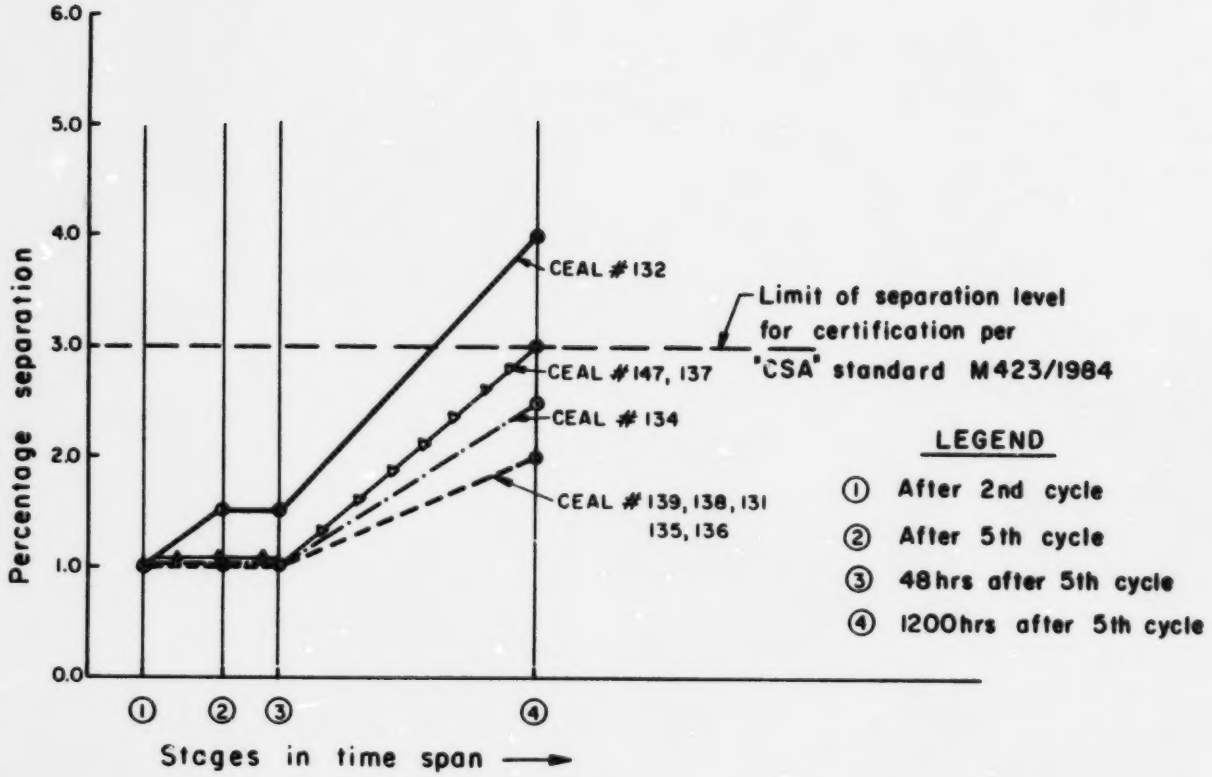

Fig. 1 - Percentage oil separation (uncovered cylinders)

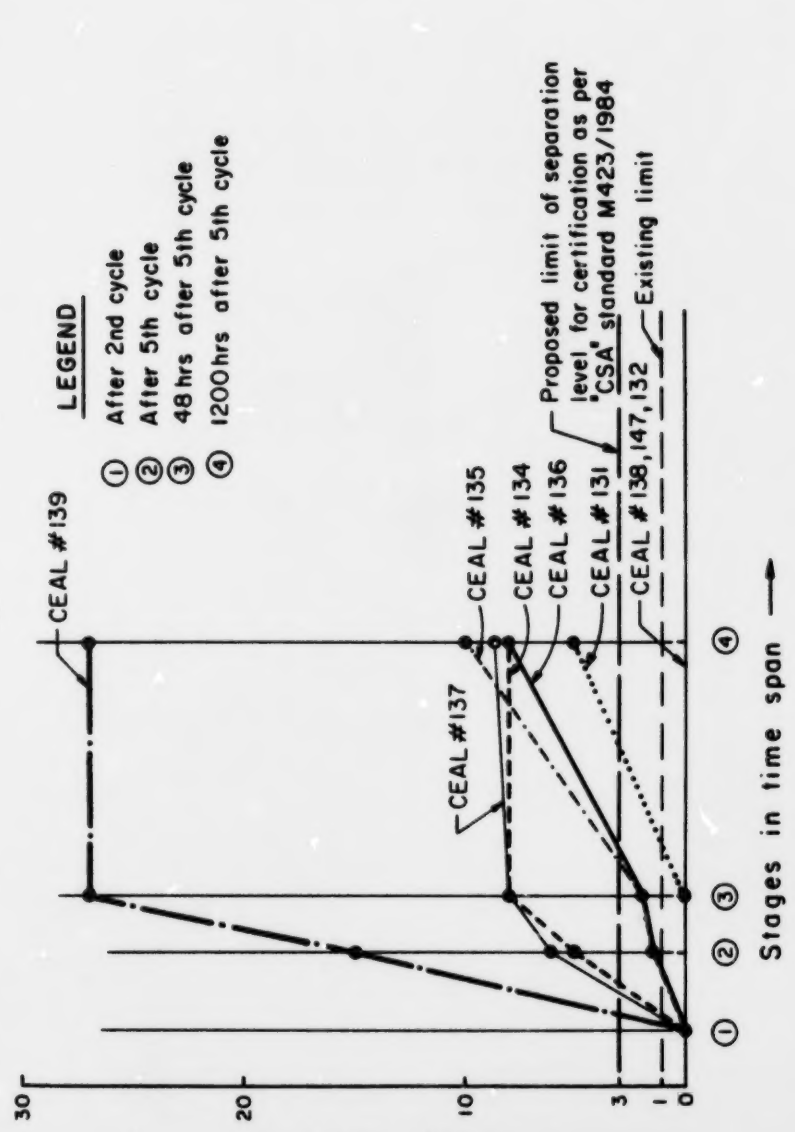

Fig. 2 - Percentage water separation (uncovered cylinders)

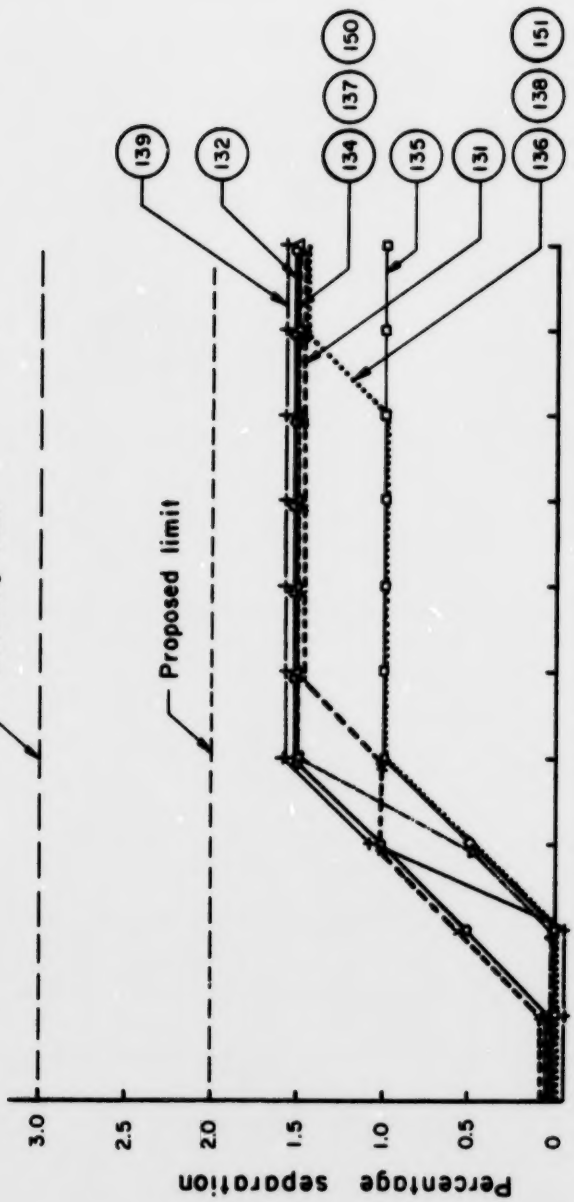

Fig. 3 - Percentage oil separation (covered cylinders)

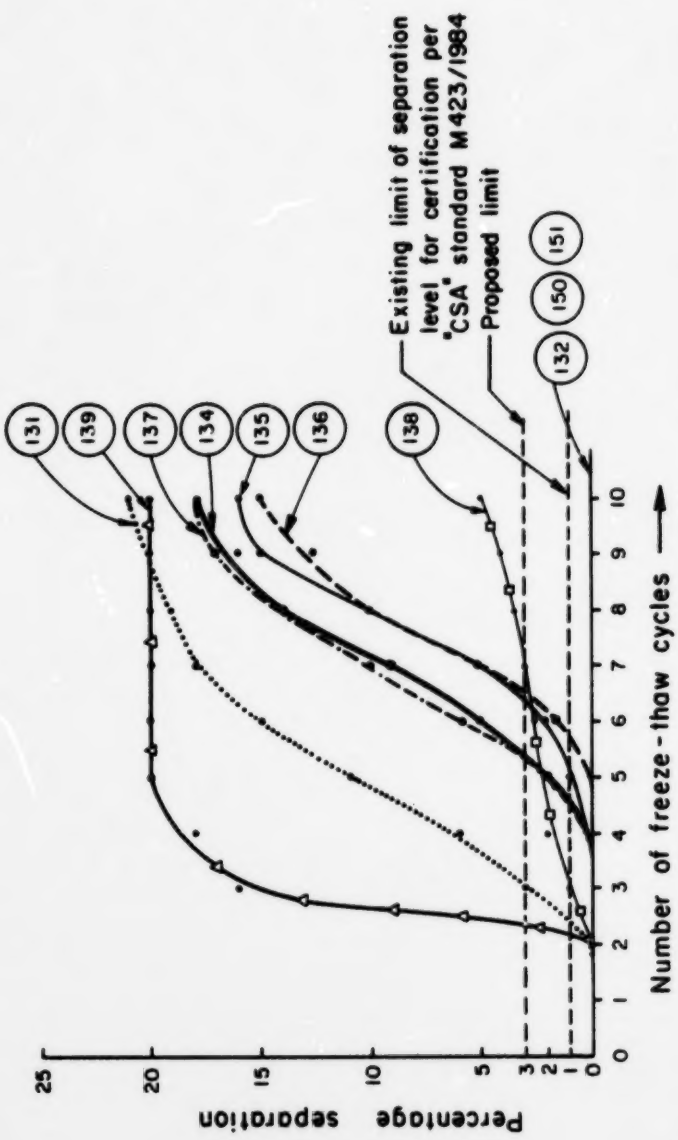

Fig. 4 - Percentage water separation (covered cylinders)